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DOI: https://doi.org/10.1029/2010JG001452

Originally published at:
Lyon, S W; Grabs, T; Laudon, H; Bishop, K H; Seibert, Jan (2011). Variability of groundwater levels and total organic carbon in the riparian zone of a boreal catchment. Journal of Geophysical Research, 116(G01020):12.
DOI: https://doi.org/10.1029/2010JG001452

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 116, G01020, doi:10.1029/2010JG001452, 2011

Variability of groundwater levels and total organic carbon in the riparian zone of a boreal catchment

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Received 16 June 2010; revised 25 October 2010; accepted 11 November 2010; published 22 February 2011.

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Citation: Lyon, S. W., T. Grabs, H. Laudon, K. H. Bishop, and J. Seibert (2011), Variability of groundwater levels and total organic carbon in the riparian zone of a boreal catchment, *J. Geophys. Res.*, *116*, G01020, doi:10.1029/2010JG001452.

1. Introduction

[2] Landscape biogeochemistry and, in particular, landscape carbon dynamics are intimately coupled to ecosystem and climatic changes. Total organic carbon (TOC), for example, is a key source of energy to the aquatic ecosystem [*Berggren et al.*, 2007]. In addition, TOC in streams and lakes has been seen to play a dominant role in determining water chemistry and quality [e.g., *Cory et al.*, 2007]. Add to this the potential role of TOC in the "aquatic conduit" of carbon [e.g., *Cole et al.*, 2007] and it becomes clear that a good understanding of the spatiotemporal dynamics of the various stores and sources of carbon in terrestrial systems is needed to gauge changes to date and to estimate or evaluate potential future scenarios of change. This need is further exemplified in northern boreal systems where the landscape terrestrial systems are typically regarded as a net sink of CO_2 from the atmosphere [*Chapin et al.*, 2000] while the landscape aquatic systems are typically regarded as a net source of CO_2 to the atmosphere [*Cole et al.*, 2007]. Boreal landscapes often contain numerous and complex interactions between terrestrial ecosystems and terrestrial hydrologic systems. The riparian zone serves as a narrow corridor in the landscape representing an important interface between these two systems where much of the terrestrial carbon reaching surface waters originates [*Bishop et al.*, 1990; *Dosskey and Bertsch*, 1994; *Hinton et al.*, 1997].

[3] The riparian zone is a strip of the landscape that serves as the interface between the hillslope (with its associated hydrobiogeochemical processes) and the river system. With respect to catchment hydrology, the riparian corridor is unique because of the zone's distinct hydrological connectivity [*Burt and Haycock*, 1996] between hillslopes and rivers and its ability to influence runoff generation [*Bishop*, 1991; *McDonnell et al.*, 1991], the hydrological response of the catchment [*Cirmo and McDonnell*, 1997; *Cloke et al.*, 2006], and solute flux [*Brinson et al.*, 1981; *Hill*, 1996; *Petrone et al.*, 2007]. Several characteristics have been used to help define the extent of this riparian zone. These focus on distinguishing riparian areas from adjacent upslope positions [*McGlynn and Seibert*, 2003] and include characteristics

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0148-0227/11/2010JG001452

such as anoxic zones [*Megonigal et al.*, 1993], gleyed soils [*Phillips et al.*, 2001], color [*Blavet et al.*, 2000], organic content [*Mitsch and Gosselink*, 1993], breaks in slope [*Merot et al.*, 1995], contributing area thresholds [*McGlynn and Seibert*, 2003], and near-surface water tables [*Brinson*, 1993]. The differences between riparian and upslope positions influence not only the hydrologic interactions but also the movement and loading of solutes to the stream network. Specifically, the riparian zone serves as the last piece of landscape with which water will interact as it transitions from being water flowing primarily *through* the landscape (i.e., shallow groundwater) to water flowing primarily *on* the landscape (i.e., stream water).

[4] *Bishop et al.* [2004] used this view of the riparian zone as a key determinant of stream chemistry to resolve part of the double paradox presented by *Kirchner* [2003], at least for a boreal forest case study. In boreal systems, upslope podzols (spodosols) and the riparian organic soils have distinct and persistent vertical patterns in soil solution chemistry, and as such, lateral flow traversing the riparian zone acquires the solution chemistry corresponding to the depth of its flow path across the riparian zone. *Burt* [2005] comments that this view may perpetuate a lumped approach by not accounting explicitly for flow pathways and the evolution of water chemistry as water progresses through the riparian zone. Increased knowledge of the spatial pattern of hydrological processes is called for in order to address the dynamic nature of biogeochemistry and hydrology within the riparian buffer zone. Recently, *Köhler et al.* [2009] presented research to address this variability in hydrological processes. Using a regression analysis, they demonstrated that the largest part of the temporal variation of stream TOC concentrations in a forested headwater stream in the boreal zone in northern Sweden may be explained with runoff and transformed air temperature as the sole input variables. Runoff is assumed to be a proxy for soil wetness conditions and changing flow pathways, which in turn caused most of the stream TOC variation.

[5] To scale up (e.g., move to scales larger than the ~1 km^2 headwater scale) modeling approaches for reproducing the observed dynamics of TOC in boreal streams, there is a need to characterize both the spatial pattern of hydrological processes and the spatiotemporal patterns of the TOC in the riparian zone. Specific to these northern Swedish boreal systems, much recent work has gone into characterizing spatial patterns in hydrologic processes over larger spatial scales. This includes isotopic tracing of flow pathways during different flow regimes [*Laudon et al.*, 2007], mapping of spatial patterns of wetness [*Grabs et al.*, 2009], and modeling of mean transit times for snowmelt water [*Lyon et al.*, 2010] for the 15 nested catchments within the 67 km^2 Krycklan catchment study area located in northern Sweden. These studies have shown great variability in hydrologic processes and responses for the mosaic of landscape characteristics present in this boreal system. While this variability could explain a large part of the variability in the stream TOC, the spatiotemporal variability and dynamics of the riparian TOC and flow pathways must be characterized and accounted for to develop distributed, physically based models that successfully couple hydrology and biogeochemistry in such landscapes [*Burt*, 2005]. The temporal and spatial variation of TOC is valuable and significant as a response to environmental signals such as changes in biological activity, soil water content, and temperature [e.g., *Lydersen*, 1995; *Hessen et al.*, 1997; *Tipping et al.*, 1999]. Characterizing spatiotemporal variability of riparian TOC and flow pathways is a promising building block for refining available modeling approaches to estimate TOC transport from the landscape to the stream network.

[6] The goal of this research was to investigate the connection between soil water TOC and the shallow groundwater table in the riparian zone through their coupled spatiotemporal variability. Specifically, are there landscape-scale and seasonal variations in the relation between water table position and soil water TOC? This was investigated by leveraging off an extensive, robust, and unique set of observations from the recently instrumented riparian observatory in the Krycklan catchment study area. This observatory was designed to facilitate the monitoring of riparian-zone soil water chemistry, shallow groundwater level, and temperature, with the explicit goal of spanning a broad range of riparian settings in this boreal system. In the current study we present measurements pertaining to soil water TOC observations and shallow groundwater level. During several field campaigns in 2008, soil water TOC at several depths in the soil profile was measured at several riparian locations. In addition to soil water sampling, shallow groundwater levels were monitored at each of these sampling locations. Spatial and temporal variability in soil water TOC was observed in conjunction with changes in the shallow water table across the landscape observed via sampling locations in the riparian observatory. This current study provides a first step toward the development of a spatially resolved understanding of riparian-zone hydrologic transport of solutes. This, in turn, may allow for characterization or parameterization of the variability present (in space and time). Such understanding and characterization could form the basis for models capable of explaining the complex patterns of stream chemistry observed in the Krycklan catchment and other boreal systems.

2. Materials and Methods

2.1. Study Site

[7] The Krycklan catchment study area is host to several multidisciplinary research projects related to water quality, hydrology, stream biodiversity, and climate effects. Of the 15 nested research catchments that comprise the study area, the main Krycklan catchment has its outlet located at 64°12′N and 19°52′E within the Vindeln Experimental Forests, which are approximately 50 km northwest of Umeå, Sweden (Figure 1). This catchment has a 67 km^2 drainage area. The region is climatically typified by short summers and long winters. Snow covers the ground on average for 171 days, from the end of October to the beginning of May [*Ottosson-Löfvenius et al.*, 2003]. The mean annual precipitation and temperature are 612 mm and about 1.7°C, respectively, with about 50% of the annual precipitation falling as snow [*Haei et al.*, 2010]. As such, the region is hydrologically dominated by this snowmelt period occurring in late spring [*Laudon et al.*, 2004; *Lyon et al.*, 2010].

[8] The upland parts of the main catchment are mainly forested with Norway spruce (*Picea abies*) in low-lying

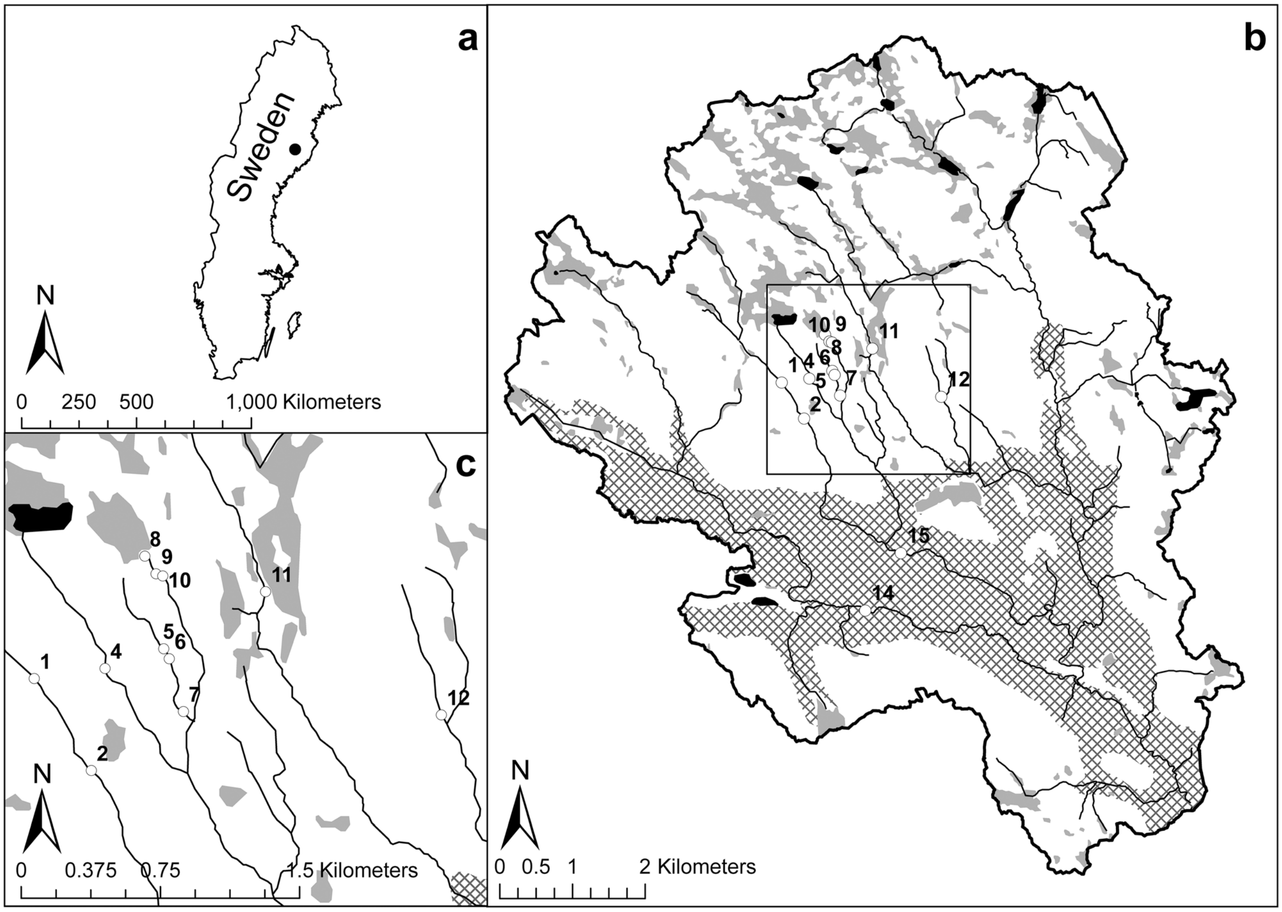

Figure 1. Site map showing (a) the location of the Krycklan catchment study area in boreal northern Sweden and (b) the positions of each of the 13 instrumented locations that comprise the riparian observatory. The catchment outlet is located at 64°12′N and 19°52′E. Lakes are in black, mire wetlands are in gray, and silt soils are indicated by cross-hatching. (c) Zoom-in on the boxed area in Figure 1b outlines the zoom-in given in Figure 1c.

areas and Scots pine (*Pinus sylvestris*) in upslope areas. Geologically, these catchments are located on the Fennoscandian shield [*Buffam et al.*, 2007]. There are also large patches of mire wetlands, predominantly in the upper part of the main catchment. In the lower regions, Norway spruce and Scots pine are also the dominant tree species, but deciduous trees and shrubs are more common along the stream channels. Glacial tills in the upper portion of the main catchment give way to deeper sorted sediments toward the catchment outlet (Figure 1). Small areas of agricultural fields are found in the lower part of the catchment.

[9] Samples considered in this current study were collected during site visits throughout 2008 (Table 1). Relative to the long-term conditions at the Krycklan catchment

Table 1. Field Sampling Campaign Dates for Manual Sample Recovery for the Observations Used in This Study[a]

Field Sampling Campaign	Dates	Average Daily Streamflow (L/s)	Percentile of Long-Term Streamflow	Average Temperature (°C)	7 Day Antecedent Rainfall (mm)
1 (May 2008)	13–17 May 2008	7.7	83rd	2.9	1.0
2 (June 2008)	20–24 Jun 2008	1.8	48th	12.7	7.6
3 (July 2008)	24–28 Jul 2008	2.5	58th	15.6	65.3
4 (August 2008)	22–26 Aug 2008	6.1	78th	12.4	15.9
5 (September 2008)	20–23 Sep 2008	1.8	48th	7.1	1.0
6 (October 2008)	21–23 Oct 2008	7.8	83rd	1.6	20.2

[a]For convenience, we refer only to the month in which the campaign occurred, given in the text. The average climatological conditions during and (in the case of rainfall) prior to the sampling campaigns is given. The percentile of long-term streamflow is computed based on the 30 year flow record at the reference subcatchment.

study area, 2008 was a fairly normal year. The average temperature for 2008 was 2.9°C and the total precipitation was 659 mm, compared to the long-term averages of about 1.7°C and 612 mm for temperature and total precipitation, respectively. To put this year and the individual sampling dates considered in the following further into perspective, the median daily streamflow for the reference 0.5 km^2 subcatchment (Kallkälsbäcken) considered in the work by *Laudon et al.* [2007] was 2.4 L/s for 2008. This median daily streamflow for 2008 corresponds to the 56th percentile of daily streamflow when considering the long term 30 year streamflow record for this reference subcatchment. Note this reference subcatchment from *Laudon et al.* [2007] is the same as the Svartberget catchment of *Bishop et al.* [1990].

2.2. The Riparian Observatory

[10] The riparian observatory is a series of instrumented locations across several riparian positions within the Krycklan catchment study area (Figure 1). Each location is instrumented with soil suction lysimeters for sampling soil water at several depths, capacitance probes for monitoring shallow groundwater levels, and thermistors for monitoring temperature at several depths. In the current study we present data pertaining to the soil water TOC measured in samples collected using the soil suction lysimeters and the shallow groundwater levels, both of which are described in detail here. All data and samples were collected at monthly intervals from May 2008 through October 2008 under various climatological and antecedent conditions (Table 1). The streamflow conditions for each site visit span a range of flow conditions in the Krycklan catchment study area.

2.2.1. Sampling of Soil Water Total Organic Carbon (TOC)

[11] In total, 13 sites were instrumented to extract soil water samples (Figure 1). Porous ceramic suction lysimeters were used to gather soil water samples within the soil profile approximately 1 to 2 m away from the streams. At each instrumentation site a pair of suction lysimeters was installed at 15, 30, 45, 60, and 75 cm below the soil surface. All lysimeters were sampled manually at a monthly interval from May 2008 through October 2008 by applying about 100 kPa (1 bar) of suction (Table 1). The collection of the samples took about 24 to 48 h per lysimeter, and prior to sample collection the lysimeters were purged. Soil water was sampled into acid-washed and Milli-Q-rinsed 0.5 or 1 L Duran glass bottles. Samples were sealed and retrieved from the field for analysis. Samples were acidified and sparged to remove inorganic carbon before the TOC was measured using a Shimadzu TOC-VPCH analyzer. The measured TOC concentrations for the water samples collected at each pair of soil suction lysimeters were then averaged. This results in one TOC concentration for each sampling level in the soil profile (5 in total: 15, 30, 45, 60, and 75 cm below the soil surface) at each instrumentation site (13 in total) for each sampling campaign (six in total for 2008) used in this study. It should be noted that TOC is composed of at least 90% dissolved organic carbon (DOC) in these boreal stream systems [*Ågren et al.*, 2007]. For the soil water TOC measures in the current study, since samples are strained to some extent by the small effective pore size of the porous cups on the lysimeters, it stands to reason that a large portion of the TOC is DOC.

2.2.2. Shallow Groundwater Observations

[12] Shallow groundwater levels were automatically recorded beginning in May 2008. Water levels were monitored using capacitance probes (TruTrack) placed inside a groundwater well screened along its length. Each well was installed to monitor groundwater levels in the upper 1 m of the soil profile. The capacitance probes were programmed to sample and store groundwater table positions at 1 h intervals. These data were then retrieved using handheld computers during site visits (Table 1). These probes have a vertical resolution of about ±1 mm, which has been improved to about ±0.2 mm in the current study using a temperature correction. To make shallow groundwater observations consistent with the manually sampled TOC concentrations, we report the monthly average values and variations across all instrumentation sites. This is a simplification of the shallow groundwater dynamics but still provides a first-order representation of temporal changes. We leave a full investigation of the spatiotemporal dynamics of the shallow groundwater table to forthcoming investigations.

3. Results

3.1. Riparian Soil Water TOC

[13] Looking across all 13 instrumented locations, there were seasonal patterns in the variability of soil water TOC with depth in the soil profile for the 2008 sampling season (Figure 2). TOC concentrations observed during May, June, and July 2008 were more constant with depth below the soil surface than those observed during August, September, and October 2008. Averaging across all depths of observation at all sampling locations, the average TOC concentration was 15.3 mg/L for May 2008 and 16.5 mg/L for June 2008. Moving into July 2008, there was a corresponding increase in soil water TOC concentrations in the upper soil layers across all instrumentation locations. There was also an increase in the standard deviation and range of measured TOC concentrations in upper soil layers across all sites. This increase in soil water TOC and variability across sites continued through September 2008. In October 2008 the average TOC concentration at the shallowest observation level (15 cm deep) reached a peak across the period of observations at 34.2 mg/L.

[14] The averaged observed TOC concentrations for each month could be modeled with varying degrees of success as a function of soil depth using an exponential decay (Figure 2). As these exponential decays are fit to the averages at given observation levels, the R^2 values (which range from 0.74 to 0.94) are inflated relative to what would be achievable by fitting an exponential decay to all the observed TOC concentrations. The rate at which soil water TOC decays with respect to depth in the soil profile reached its highest values during August and September 2008. This exponential decrease in TOC soil water concentrations with depth in the soil profile was similar to the profiles along a single hillslope transect reported by *Bishop et al.* [2004] and *Köhler et al.* [2009].

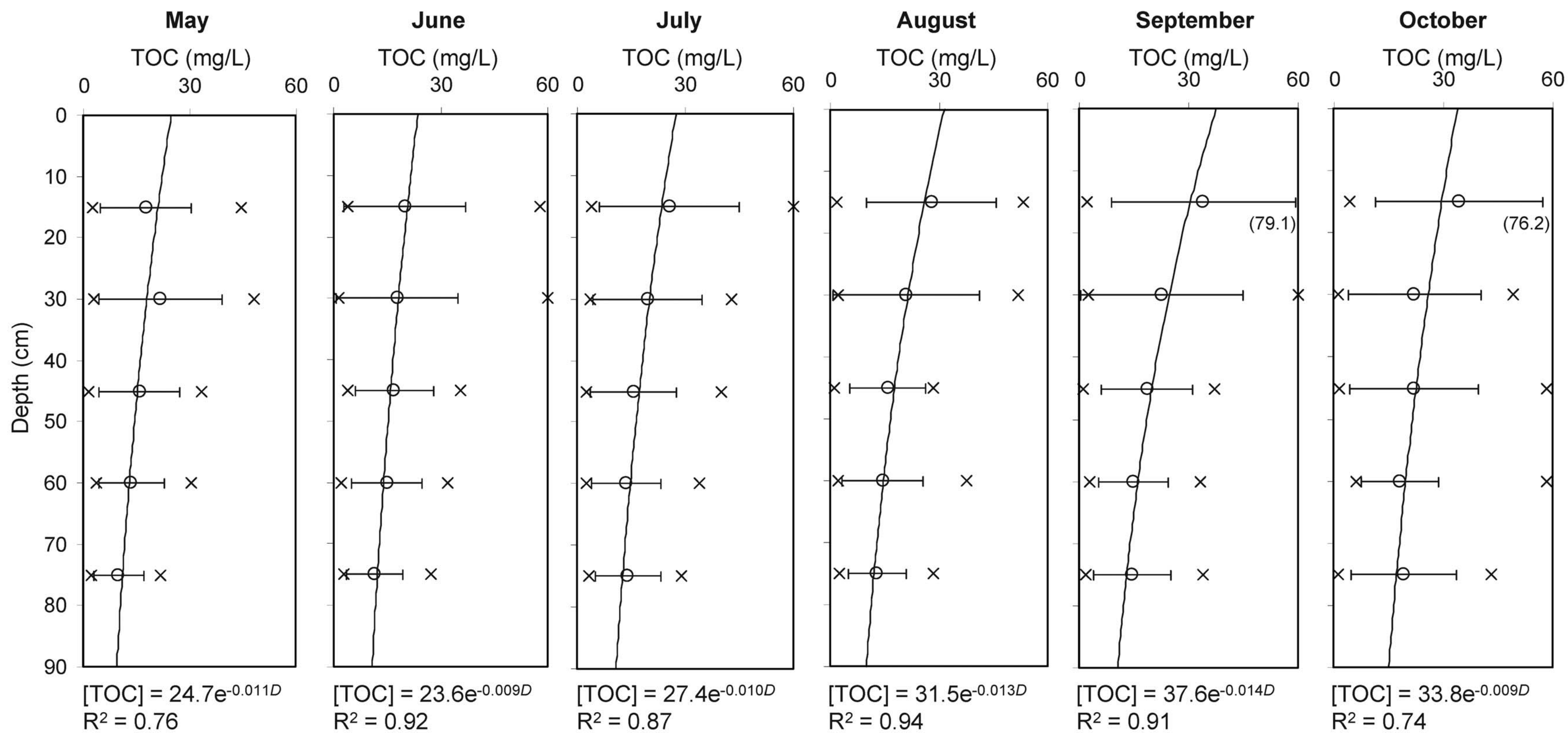

Figure 2. Soil water total organic carbon (TOC) variability between the monthly sampling campaigns for all sites in the riparian observatory. Points represent the average and bars show 1 standard deviation at a given depth of observation across all 13 riparian observatory sites. Crosses show the relative maximum and minimum soil water TOC concentration across all samples collected at each depth. Numbers in parentheses indicate concentrations observed not fitting with the scale of the plots. The reported exponential decays are fit to the averages, and as such, R^2 values are inflated relative to what would be achievable by fitting an exponential decay to all observed TOC concentrations.

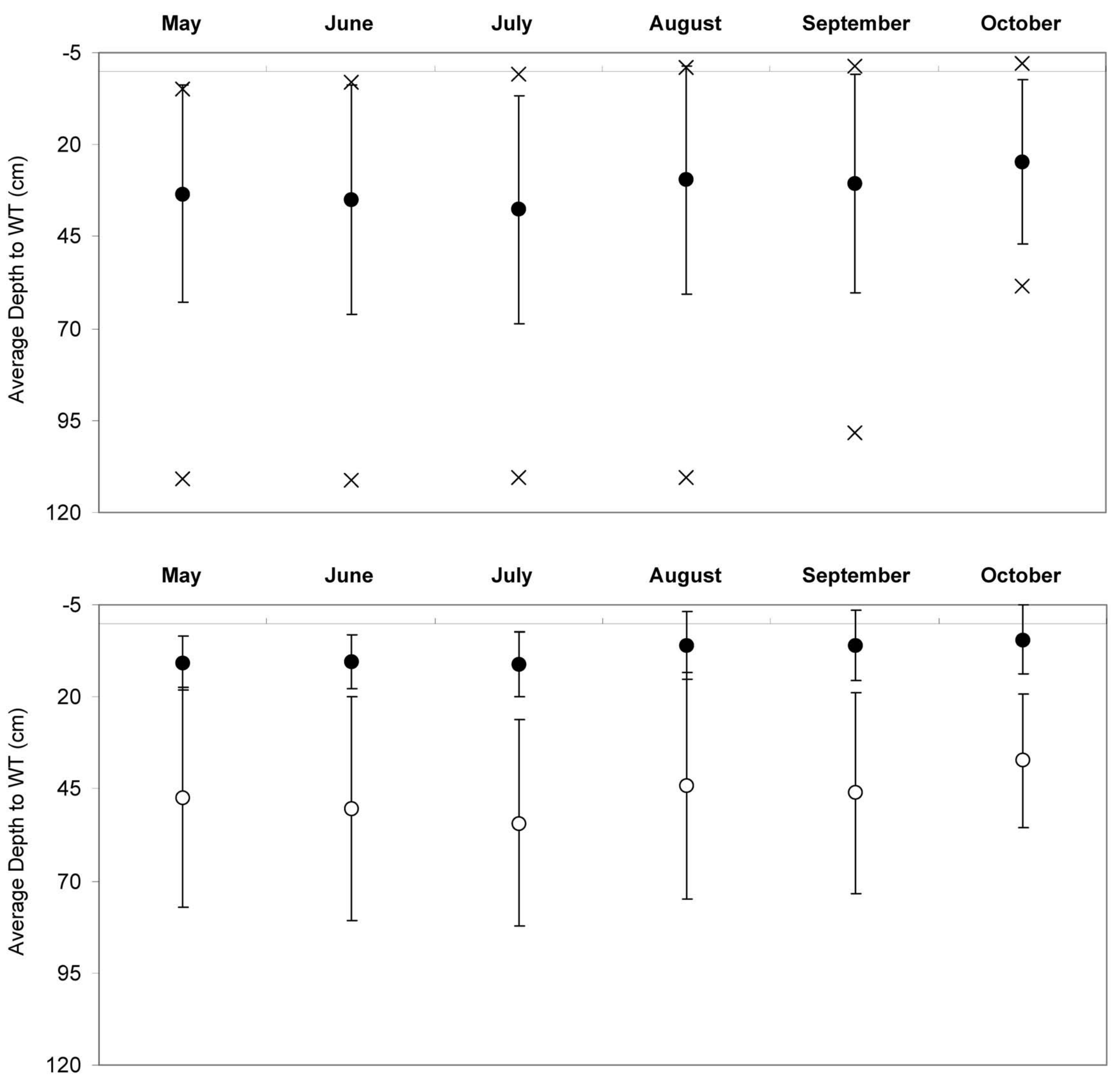

Figure 3. Monthly average shallow water table (WT) (top) across all 13 sites instrumented in the riparian observatory and (bottom) for sites grouped according to local slope, with filled symbols showing the average for sites with a slope of <5% and open symbols showing the average for sites with a slope of >5%. Bars show 1 standard deviation and crosses show maximum and minimum monthly average depths to WT observed across the sites.

Table 2. Monthly Statistics for Shallow Groundwater Tables for the Riparian Observatory Based on 1 h Interval Observations[a]

Riparian Site ID	May		June		July		August		September		October	
	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD
1	53.2	3.1	55.5	4.8	56.9	6.5	49.1	6.3	53.9	2.9	48.3	6.2
2	12.3	1.2	13.0	4.6	16.4	7.6	6.9	3.8	7.7	1.9	4.7	2.5
4	110.9	0.2	111.0	0.6	110.4	2.3	110.4	1.3	98.6	19.2	58.6	3.9
5	16.1	0.8	15.0	3.2	20.9	5.8	13.2	3.6	15.9	2.3	12.0	3.3
6	18.6	0.5	19.8	2.3	22.7	5.6	14.4	5.0	16.3	2.1	12.9	5.8
7	30.3	1.4	31.6	3.6	45.4	10.3	28.0	3.4	28.0	2.3	25.3	3.4
8	7.2	0.9	7.5	3.7	8.0	4.3	−0.1	1.7	−0.6	1.0	−2.0	1.5
9	45.1	3.1	52.5	5.6	56.6	7.0	39.7	5.2	41.8	5.9	42.4	5.8
10	23.0	0.1	22.1	1.1	23.4	1.9	21.7	1.7	22.0	0.8	20.3	1.3
11	6.6	1.0	6.9	2.3	7.1	2.5	2.6	1.9	2.7	1.0	1.1	1.5
12	54.5	7.4	66.1	5.5	69.0	10.5	54.3	3.7	62.2	4.4	54.3	8.3
14	5.0	0.4	3.0	0.7	0.9	0.8	−0.9	0.6	−1.5	0.3	−1.9	0.2
15	50.4	1.0	51.2	3.3	51.5	7.5	45.3	5.7	51.8	2.7	44.8	6.1

[a]SD, standard deviation. Site IDs are not numbered sequentially.

3.2. Riparian Shallow Groundwater

[15] On the basis of the record of observation considered in this study, the shallow groundwater table was fairly close to the soil surface within the riparian zone (Figure 3, top). The average depth to water table across all locations for each month was within 45 cm from the soil surface and was skewed toward shallower values. This was evident, as the minimum depth to water table observed (upper cross in Figure 3, top) was often about 1 standard deviation from the average depth to groundwater table observed within the riparian zone across all locations. The general wetness and nearness of the water flow pathways to the surface of the riparian corridor in this boreal landscape were indicated by this consistently shallow water table. There was, of course, within-month variability in the shallow groundwater levels across the riparian observatory as indicated by the standard deviation of the observed 1 h interval data (Table 2, Figure 3, top). In addition, the last 3 months (August 2008 through October 2008) had average water tables that were closer to the soil surface than the first 3 months of observation. The maximum and minimum average depth to shallow groundwater table across all 13 observation locations decreased (i.e., got closer to the soil surface) and the standard deviation across all locations decreased over the period of observation. This indicates that the water tables were relatively closer to the soil surface overall, and more often as the summer progressed.

[16] Any spatial variability in the monthly average groundwater table can be partially explained by the local slope for each observation location (Figure 3, bottom). For example, using the ground surface local slope at each observatory site estimated from a 5 m resolution digital elevation model, sites can be grouped to those with a local slope of less than 5% (n = 5) and sites with a local slope greater than 5% (n = 8). There were significantly different ($p < 0.05$) monthly average depths to shallow water tables between the low-slope and the high-slope riparian positions. That is, sites where the local slope is steeper (>5%) have deeper water tables than sites where the local slope is less steep (<5%). This is somewhat similar to the catchment-scale findings of *Lyon et al.* [2010], indicating a strong connection between topographic gradients and the movement of water through the Krycklan catchment study area.

3.3. Soil Water TOC in Relation to Shallow Groundwater

[17] The average soil water TOC across all observations for each instrumentation location in the riparian observatory can be related to the monthly average depth to groundwater table at the location (Figure 4). This allows investigation of the intersite spatial variability in TOC as a function of the wetness of the riparian zone. In general, the average TOC in the soil profile increased with increasing groundwater level. For sites with groundwater tables very close to the ground surface, however, TOC values decreased again. That is, when the average water table was close to the soil surface, average soil water TOC concentration was lower (open circles in Figure 4). Note, however, that this general trend is based on only a few sites. The average TOC in the soil profile tended to reach a maximum when the average monthly water table was about 5 cm from the soil surface. There was a decrease in TOC with water table (below 5 cm), which can be modeled adequately across all months using an exponential decay. This exponential decay correlated most strongly during August (R^2 = 0.88) and was weakest during May (R^2 = 0.56). Note that while there is one site with a consistently low water table and TOC soil water concentration, removing this site from the analysis in Figure 4 does not fundamentally alter the form or fit of this exponential decay. As such, this site, while possibly an outlier, does not dominate the fitted relationship.

[18] To test the reliability of the exponential relations found between the average water table positions and the average soil water TOC concentrations, we perform a leave-one-out cross validation. This type of cross validation omits one site from the analysis and then estimates its value (here, the average soil water TOC) using the relationship defined by the remaining sampling locations. This procedure was repeated for each site and across all sampling periods. A cross-validation error was then calculated as the difference between the actual average soil water TOC and the value estimated (Figure 5). It can be seen that the cross-validation error is relatively larger for sites where the average water table is closer to the soil surface. This is expected given the scatter around the exponential relationships shown in Figure 4. The overall magnitudes and ranges of cross-validation error between the individual sampling

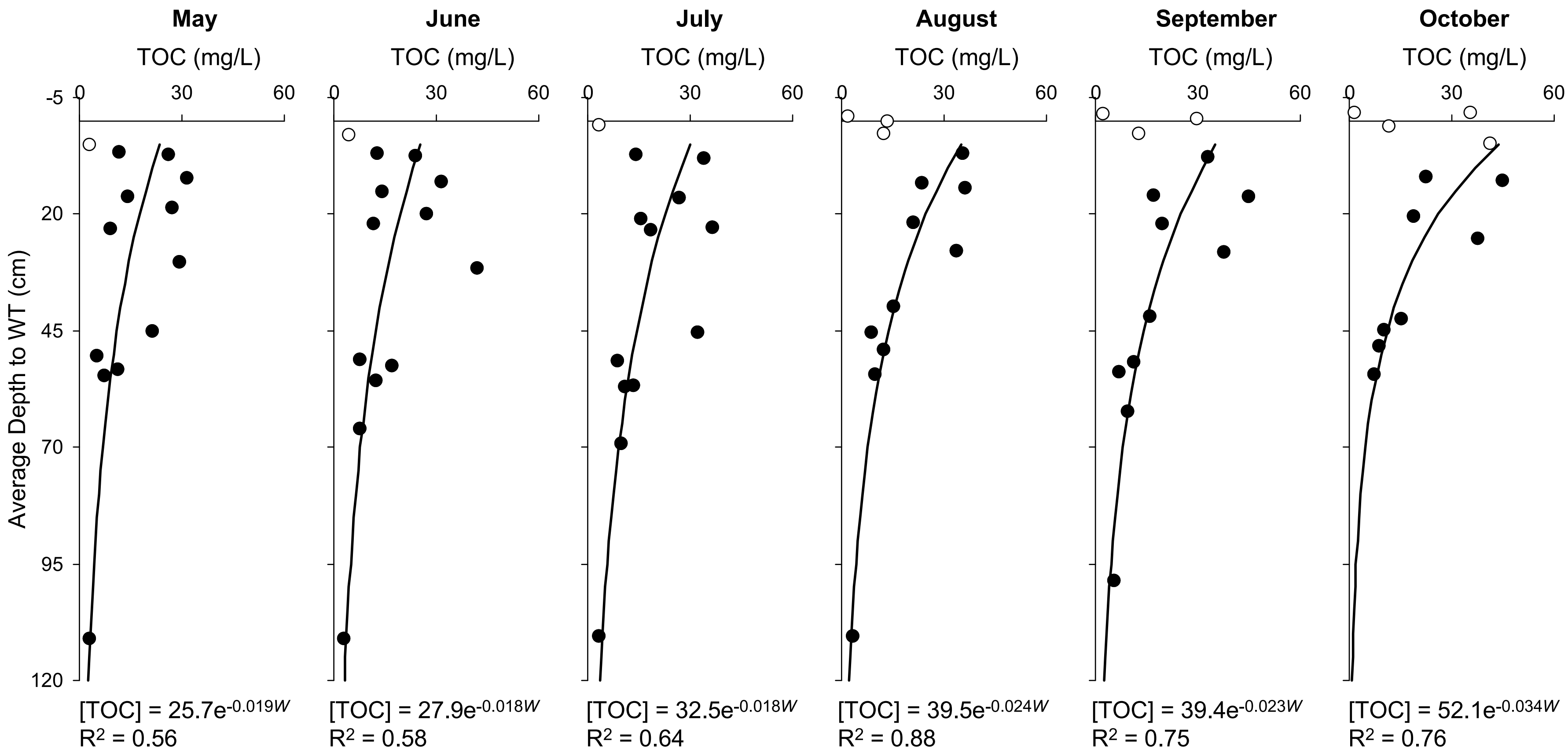

Figure 4. Average soil water TOC across the entire soil profile at each observation location in relation to the monthly average shallow groundwater table at the location. Open symbols are locations where the monthly average water table is within top 5 cm of the soil profile and are excluded from the exponential model.

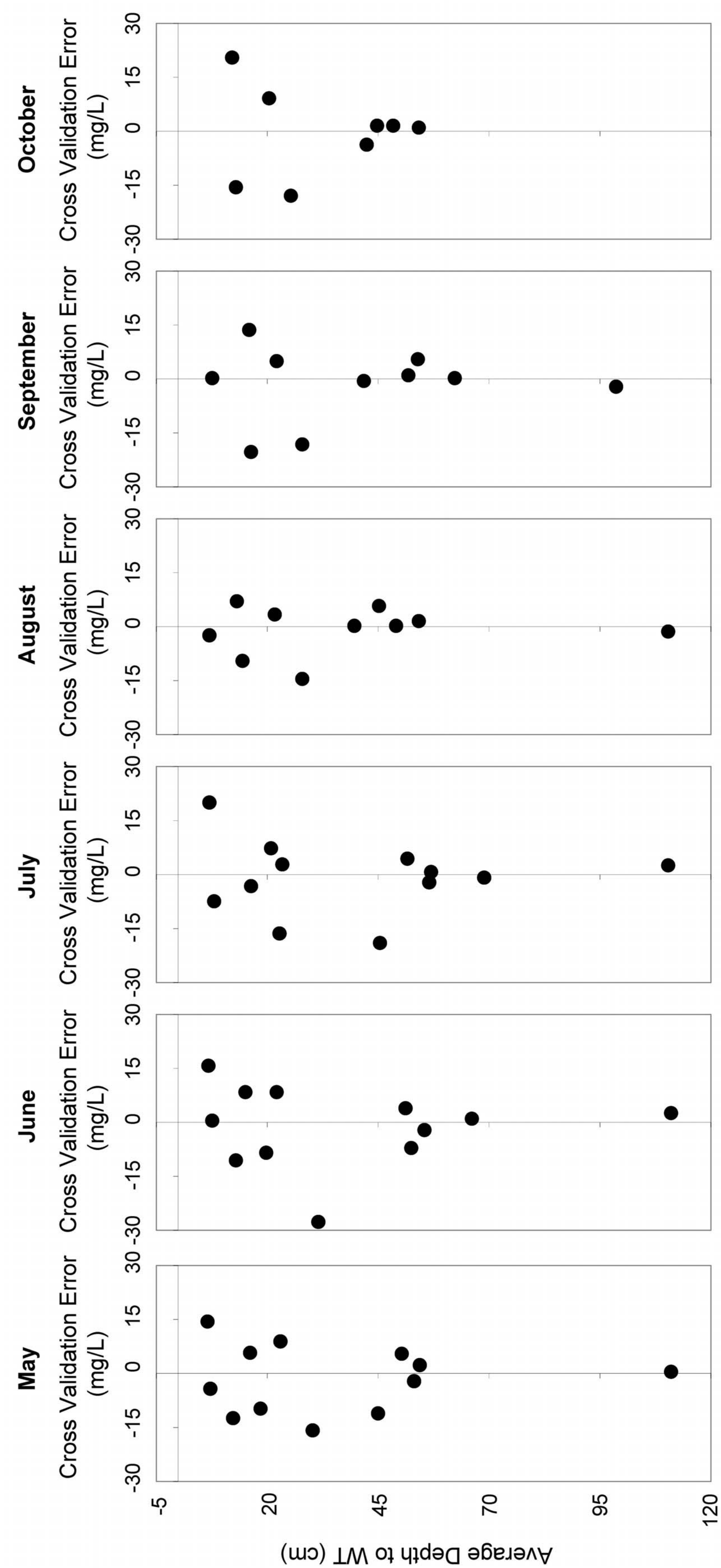

Figure 5. Leave-one-out cross validation error based on exponential relationships between average soil water TOC across the entire soil profile and monthly average shallow groundwater table.

campaigns are rather consistent. Further, the exponential relationships shown in Figure 4 are not contingent on the potential "outlier" since this site has a low cross-validation error when being predicted with the actual value left out of the analysis.

4. Discussion and Concluding Remarks

[19] Riparian hydrology and TOC concentration were clearly linked. Spatiotemporal variability in soil water TOC within the riparian observatory was related to these shallow groundwater table dynamics (Figure 4). Spatial variability in the hydrologic system was characterized by the variation in shallow water table positions across the different observation sites. This variability influences the flow pathways that are active within the riparian zone. This, in turn, influences the movement of TOC through the riparian zone. For the locations included in this riparian observatory, it seems reasonable from the observations that high groundwater levels have been important for shaping the organic carbon buildup in the riparian zone. The higher the groundwater (closer to the soil surface), the higher the soil water TOC concentration. This general trend appears to hold until the groundwater table moves into the uppermost 5 cm of the soil profile.

[20] It is likely that flushing or dilution effects dominate the soil water TOC concentrations in the top 5 cm of soil. Moreover, there could be additional biological controls influencing the riparian TOC concentrations in combination with such hydrologic controls. Mechanistically, riparian TOC concentrations and profiles could be influenced by prolonged soil wetness, elevated soil temperature, combinations of both, or seasonality of plant growth, which influences cation uptake and/or organic matter quality [*Christ and David*, 1996]. Regardless, the spatiotemporal dynamics in both the soil water TOC and the shallow groundwater must be adequately characterized to properly represent riparian-zone TOC dynamics. The coupled dynamics of these hydrologic and biogeochemical systems raise questions about the ability of simple lumped and/or temporally static models to accurately predict in-stream TOC concentrations. By "lumped" we mean either lumped with respect to the TOC concentration profile or lumped with respect to hydrologic regime. This is similar to the result seen by *Köhler et al.* [2009], where a simple convolution model, based on a static soil water TOC concentration profile, performed well but allowed for no possibility of capturing variations in different carbon pools or systematic changes in soil chemistry or flow pathways that may be caused by long-term variations in the riparian water balance (such as increased evaporation). Further, the work by *Seibert et al.* [2009] demonstrated the need for seasonal variations in soil water TOC profiles in order to preserve observed stream concentrations. This variation in TOC across the landscape between seasons has been seen in other studies as well [e.g., *Clark et al.*, 2005]. The variability found in the soil water TOC profile within and between months (Figure 2) highlights the need for information and understanding beyond a single, "representative" transect approach to model stream TOC concentrations at a catchment scale.

[21] With respect to spatiotemporal dynamics in the shallow groundwater table, there is a mosaic of hydrologic response and hydrologic spatial variability seen in boreal landscapes. In particular, for the Krycklan catchment study area, *Laudon et al.* [2007] used stable water isotopes to identify dominant runoff (quick-flow) flow paths through the landscape. *Lyon et al.* [2010] further demonstrated that there is a strong seasonal component to the transfer of water through the landscape, which is also coupled to variations in landscape characteristics. Their work also demonstrated a strong control of landscape slopes on the movement of water at the catchment scale. *Grabs et al.* [2009] incorporated the spatiotemporal dynamics of the shallow groundwater table into a dynamic wetness index that allowed accurate prediction of wet areas within both the landscape and the riparian corridor. These previous and ongoing hydrological studies, based on both field observations and modeling approaches, aid in the understanding of how water moves into the riparian corridor from upslope or hillslope positions and help describe the development of flow pathways through the riparian zone itself. This can be used as the basis of a model capable of identifying and modeling the spatiotemporal evolution of flow pathways through the riparian corridor [e.g., *Seibert et al.*, 2009]. Such an approach, which allows for increased representation of the shallow groundwater spatiotemporal dynamics, is required to accurately estimate not only the hydrologic response in this boreal system but also the hydrologic transport of solutes from the riparian zone into the stream network.

[22] For sites where the monthly average shallow groundwater tables in the riparian zone were closer to the soil surface, there was an increase in the average soil water TOC (Figure 4). This is consistent with the conceptual approach put forward, for example, by *Bishop et al.* [1990] and *Seibert et al.* [2009]. When water tables are, on average, closer to the soil surface, they incorporate more superficial flow pathways and, as such, flow in more TOC-rich horizons of the soil profile (Figure 2). This could lead to higher TOC values at the sampling locations. Of course, this is true only up to a certain level. As the average water table reaches the uppermost layers of the soil profile (i.e., top 5 cm), there is an observed decrease in the soil water TOC concentrations (based on a few sites). This may be attributed to the incorporation of (to a limited amount) overland flow or direct rainfall leading to a dilution of TOC in the uppermost layers of the soil. This decrease may also have to do with the flushing of TOC from the upper soil profile or with decreases in biological activity. Sites where the water table is persistently close to the soil surface may more often experience continuous lateral flows through upper horizons. Previous studies have highlighted the importance of changing flow pathways and the extent of riparian zones in boreal regions for changing concentration and character of soil TOC [*Dosskey and Bertsch*, 1994; *Hinton et al.*, 1997; *Bishop et al.*, 1994; *Ågren et al.*, 2008, 2010]. The riparian zone has also been found to control other biogeochemical compounds in the Krycklan catchments, including CO_2 [*Öquist et al.*, 2009], lead [*Klaminder et al.*, 2006], mercury [*Bishop et al.*, 1995], aluminum [*Cory et al.*, 2007], and dissolved organic nitrogen [*Petrone et al.*, 2007].

[23] In addition to the interplay between the biogeochemistry and the hydrology in the riparian zone, several physical, chemical, and biological factors are likely at work concurrently to control the concentration of TOC in the soil

solution [e.g. *David and Vance*, 1991; *Tipping et al.*, 1999; *Mulholland*, 2003; *Köhler et al.*, 2008]. The observations and characterizations made in this current study begin to lay the basis for modeling the relationship between flow pathways and water chemistry as water progresses through the riparian zone [*Burt*, 2005]. This basis comes from the unique design of the riparian observatory. Limited data sets exist for looking at both the spatial and the temporal dynamics of the hydrologic transport of solutes across the scale of a catchment. As such, it is often necessary to estimate scaling laws or patterns of chemical loading from a few field observations. The spatially distributed sampling of flow paths and soil profile chemistry present in the riparian observatory integrates both hydrologic and biogeochemical aspects of TOC (the focus of this current study). This allows for further development and testing of distributed, physically based models that incorporate a spatially resolved understanding of the riparian control on TOC in this and similar boreal landscapes.

[24] **Acknowledgments.** The lead author (S.L.) would like to acknowledge support in the form of funding from the Swedish Research Council VR and the Bert Bolin Centre for Climate Research, which is supported by a Linnaeus grant from the VR and The Swedish Research Council Formas. We also acknowledge the support to the Krycklan Catchment Study from the VR, MISTRA Future Forests, and Formas. The riparian observatory is funded by the Kempe foundation and the Swedish Research Council (VR; grant 2005-4289).

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